ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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INTRODUCTION

Electrochemical impedance spectroscopy allows access to the complete set of kinetic characteristics of electrochemical systems, such as rate constants, diffusion coefficients, and so on, in a single variable-load experiment. It is restricted to characteristics that describe system behavior in the linear range of electrical excitation, for example, when it can be approximated by ordinary differential equations. It can be contrasted with other methods where explicitly nonlinear properties are investigated, such as cyclic voltammetry.

A requirement for linear behavior is a voltage excitation below 25 mV for experiments at room temperature or less than k_BT/e, in general, where the $V(I)$ dependency of charge-transfer reactions can be approximated as linear. Some relevant parameters remain constant over a wide range of conditions, however, and, once found under linear conditions, can then be applied to model much wider range response. Example of such parameters would be the ohmic resistance of electrolytes or the thickness of passivating films on an electrode.

While impedance spectroscopy shares the variable-load experimental method with many other linear-excitation electrochemical techniques, it also involves the transformation of time-domain signals and response to the frequency domain and the calculation of the relevant impedance, a complex quotient of voltage divided by current. It thus involves impedance calculation from the results of time-domain excitation of the system at fixed frequencies. Although "impedance" is often characterized as "complex impedance," this is unnecessary since it is an intrinsically complex quantity. Its behavior over a range of frequencies forms an impedance spectrum, leading to impedance spectroscopy.

Model creation and visualization by approximation with discrete circuit elements when possible can greatly simplify treating otherwise intractable complex systems involving multiple different processes. Further analysis is then aimed at deriving system parameters from an experimental impedance spectrum, typically by developing a model function connecting the impedance spectrum with appropriate system parameters. Such models are also usually much simpler in the frequency domain than they would be in the time domain for the same system, which can lead to parameter optimization even for quite complex systems that is easily achievable with existing computing systems.

Impedance spectroscopy is an extremely wide field and its scope is described in detail in Barsukov and Macdonald (2005), Stoynov et al. (1991), and Orazem and Tribollet (2008). While another article in this work discusses impedance spectroscopy of dielectrics and electronic conductors, IMPEDANCE SPECTROSCOPY OF DIELECTRICS AND ELECTRONIC CONDUCTORS, here we primarily deal with its application to materials containing mobile ions, although much of the present discussion is independent of those specific elements in the material that lead to dispersive behavior. The aim of this work is to provide a basic introduction to the technique, such as its principles, mathematical approaches for developing model functions for most common systems, analysis of the experimental data to obtain system parameters, and the basics of experimental implementation.

PRINCIPLES OF THE METHOD

Basic Concept of Electrical Impedance

The simplest relationship between voltage and current for electric elements is the Ohm's law, $I = V/R$, where element resistance R is dependent on neither I nor V and can be found by simply applying constant current and measuring resulting voltage across the resistor. However, nature contains not only energy dissipative elements but also energy storage elements. Current or voltage dependence of such elements as capacitors and inductors cannot be directly expressed by Ohm's law, because of time dependence ($I = C\,\mathrm{d}V/\mathrm{d}t$, $V = L\,\mathrm{d}I/\mathrm{d}t$) and the relationship between voltage and current that requires a differential equation. Finding parameter values (in this case C and L) require observing the system under variable voltage and current conditions and over a period of time, which makes system response analysis complex, especially if multiple components are present.

Fortunately, there is an indirect way to apply Ohm's law-like treatment to time-dependent systems, because all linear differential equations can be transformed into the Laplace-domain where they become ordinary equations but in terms of "complex frequency" variables, $s = \mathrm{Re} + i\omega$, where $i = \sqrt{-1}$ (sometimes also denoted as "j") and ω is the circular frequency, related to usual frequency f as $\omega = 2\pi f$. For example, on taking the Laplace transform L of $i(t) = C\,\mathrm{d}v(t)/\mathrm{d}t$ gives

$$I(s) = -C(v(0) - sL(v(t), t, s)) \tag{1}$$

Under the condition where there is no energy stored in the system before the test, $V(0) = 0$, and writing the voltage in the Laplace domain, $L(v(t), t, s)$, as $V(s)$, we get

$$I(s) = CsV(s) \tag{2}$$

This is equivalent to Ohm's law, which becomes obvious if we make a definition, $Z(s) = 1/Cs$ that turns the equation into

$$I(s) = \frac{V(s)}{Z(s)} \tag{3}$$

Here, $I(s)$ and $V(s)$ are complex current and voltage, $Z(s)$ is the complex equivalent of resistance called "impedance,"

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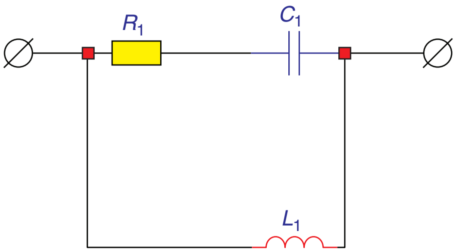

Figure 1. Example of a serial/parallel circuit.

and s is the complex frequency. This simplification for solving electric circuits and the definition of impedance was first given by Oliver Heaviside in 1880.

Conveniently, having the expression for impedance of simple element ($Z_R(s) = R$, $Z_L(s) = sL$, and $Z_C = 1/sC$), we can derive the impedance of any complicated circuit, remembering that the combination of impedances in a circuit follows the same rules as combination of resistors. So instead of first making a very complex differential equation and then applying the Laplace transform to it, we could define equations directly in the Laplace domain, by following a simple rule that for serial elements the impedances add up and for parallel elements the admittances Y (defined as $Y(s) = 1/Z(s)$) add up. Let us use an example of a circuit shown in Figure 1.

First we find impedance of section R_1 and C_1, which are in series. The impedance of this section will be $Z_1(s) = R_1 + 1/C_1 s$. The impedance of an inductive element parallel to it is $Z_2(s) = L_1 s$. Now we can turn both of these impedances into admittances so that we can use the rule about adding parallel admittances: $Y_1 = 1/Z_1 = 1/(R_1 + 1/C_1 s)$ and $Y_2 = 1/L_1 s$. Now we get the admittance of the total circuit as the sum of the parallel section admittances as $Y = Y_1 + Y_2 = 1/L_1 s + 1/(R_1 + 1/C_1 s)$. Now converting it back to impedance as $Z = 1/Y$, we get the impedance for the whole circuit:

$$Z(s) = \cfrac{1}{\cfrac{1}{L_1 s} + \cfrac{1}{R_1 + \cfrac{1}{C_1 s}}} \tag{4}$$

Measuring Impedance Values

In many practical cases, there is a need to solve an inverse problem. We have an actual electrical circuit but the values of the parameters of the circuit are not known. Since we know the relationship between the impedance function $Z(s)$ and the parameters, we could find the parameters if the impedance function is also known. How can we find it experimentally?

The first thought is that since we have the relationship $Z(s) = V(s)/I(s)$ we could experimentally measure $I(s)$ and $V(s)$, which would give us the desired function. Indeed, it is possible to collect a set of time domain measurements of $i(t)$ and $v(t)$, and then use a Laplace transform to convert the data to Laplace domain. However, this transformation requires large data amounts and computing power and is prone to high noise sensitivity and integration problems; so this direct method is only practical for simpler systems.

Historically, an approach that employs periodically repeating excitation $v(t)$ has been used instead, which does not require data collection at multiple time-points and was, in fact, used long before computers existed. This method benefits from the fact that after periodic excitation has been applied for a time much more than the time constant of the system under test, the exponential components of the response function $i(t)$ decline and become negligible. This means that if input $v(t)$ is a sinusoid, the response will also be a sinusoid, although changed in magnitude and shifted in phase. For a single-frequency sine wave applied as an excitation to a circuit

$$v(t) = V_m \sin(\omega t) \tag{5}$$

where the circular frequency $\omega \equiv 2\pi f$ is defined from the base frequency f, and after the stabilization time the response current will be observed as

$$i(t) = \mathrm{I}_m \sin(\omega t + \theta) \tag{6}$$

Here θ is the phase difference between the voltage and the current in radians (from 0 to 2π). Since both magnitude and phase can be measured directly using analog equipment, this approach already allowed impedance measurements in the eighteenth century.

To connect the phase and the magnitude of a sine wave with the impedance function we discussed in the previous section, we can take advantage of the periodicity of both signals and use Fourier transformation to transform both input $v(t)$ and response $i(t)$ into the frequency domain, $I(i\omega) = F(i(t))$, where F denotes the Fourier transformation. Since Fourier transformation deals with periodic functions, it does not contain a real part in its transform variable and so complex frequency will be just $i\omega$. It is the same frequency as used in Equations 4 and 5. Applying Fourier transformation to these equations gives $V(i\omega)$ and $I(i\omega)$ as $V_m\pi$ and $I_m\pi\ \exp(i\theta)$, respectively. Since Fourier transformation has the same property as Laplace transform of transferring differential equations into linear equations (only for periodic signals), it also maintains the Ohm's law-like relationship between excitation and response, $I(i\omega) = V(i\omega)/Z(i\omega)$.

Substituting the values for complex current and voltage for a single sine wave into this equation, we obtain the desired equation for the impedance $Z(i\omega)$ from the magnitude of sine waves V_m, I_m, and the phase shift θ, measured using analog means

$$Z(i\omega) = V(i\omega)/\mathrm{I}(i\omega) = \mathrm{V}_m \mathrm{I}_m \exp(i\theta) \tag{7}$$

To help understand the notations used in the impedance literature, we should mention that complex numbers, historically, have also been represented as phase angle and modulus. When a complex number is graphically represented as a point in the XY coordinate system where $X = \mathrm{Re}(Z)$ and $Y = I_m(Z)$, the phase θ will be the angle between the X-axis and the vector, and modulus $|Z|$ will be the length from the center to the point with coordinates X and Y. This defines the relationships $\theta = \tan^{-1}(I_m(Z)/\mathrm{Re}(Z))$ and $|Z| = [\mathrm{Re}(Z)^2 + I_m(Z)^2]^{1/2}$.

Impedance Spectrum

What can be expected from the values of $Z(i\omega)$ obtained from the experiment, in particular how will they depend on the circular frequency ω? This can be easily checked using the equations for $Z(s)$ that we derived in the first section, now substituting $i\omega$ instead of s. For the base elements, $Z_R(s)=R$, $Z_L(s)=sL$, and $Z_C=1/sC$ becomes $Z_L(i\omega)=i\omega L$ and $Z_C=1/i\omega C$.

The same substitution applies for more complex functions. For example, the function for the circuit used in Figure 1 becomes

$$Z(i\omega)=\cfrac{1}{\cfrac{1}{L_1(i\omega)}+\cfrac{1}{R_1+\cfrac{1}{C_1(i\omega)}}} \tag{8}$$

To analyze the properties of an unknown system, it is useful to graphically represent impedance functions at multiple frequencies. This is known as an impedance spectrum. Since we are dealing with complex numbers $Z(i\omega)=\mathrm{Re}+iIm$, we need to visualize not only the real part but also the imaginary part. The most commonly used plots for this purpose are Bode plots, where $\mathrm{Re}(\omega)$ and $Im(\omega)$ are plotted separately versus $\ln(\omega)$ or $\log(\omega)$, or the so-called Nyquist plot (actually a misnomer; see Barsukov and Macdonald, 2005), where $-Im(\omega)$ versus $\mathrm{Re}(\omega)$ is plotted, while frequency is implied (higher frequency is on the left). The scales of the X- and Y-axes should be the same to avoid distortion of the elements shape.

A Nyquist plot allows one to identify the elements present in the circuit from the shape of the profile. The basic elements will appear on Nyquist plot as follows: resistor as a shift on the X-axis, capacitor as a vertical line in a direction of increasing of $-Im$, inductor as a vertical line in a negative direction (increasing Im), and resistor in parallel with a capacitor as a semicircle. Inductive effects are rarely observed in electrochemical systems below frequencies of 10 kHz. An example circuit that exemplifies all of the elements common in electrochemistry is given in Figure 2.

Using the rule for adding serial impedances, we get $Z_1(s)=R_{\mathrm{ser}}+1/C_{\mathrm{ser}}s$ for R_{ser} and C_{ser}.

For the parallel combination R_1 and C_1, we use the rule about adding the admittances to find its admittance $Y_2(s)=1/R_1+C_1s$. Converting back to impedance $Z_2(s)=1/Y_2(s)=1/(1/R_1+C_1s)$.

Finally, adding Z_1 and Z_2, which are in series with each other, we get the total impedance as given in Equation 9. To calculate the impedance values at different frequencies, we will assume periodic excitation and substitute $s=i\omega$.

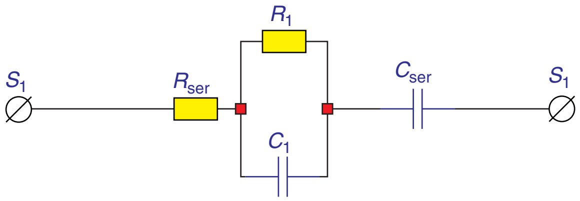

Figure 2. Example of a serial/parallel circuit.

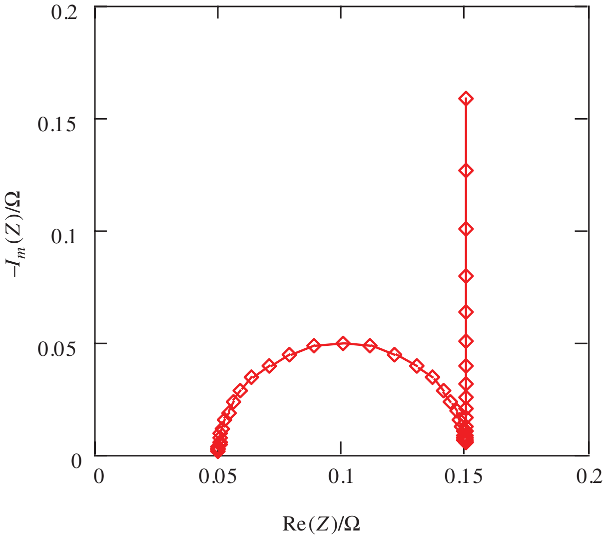

Figure 3. Impedance spectrum of the circuit in Figure 2 in the frequency range from 100 kHz to 0.1 Hz.

$$Z(\omega)=Z_1(\omega)+Z_2(\omega)=\mathrm{R}_{\mathrm{ser}}+1/\mathrm{C}_{\mathrm{ser}}i\omega+1/(1/R_1+C_1i\omega) \tag{9}$$

For a numerical example, we can use values of parameters $R_{\mathrm{ser}}=0.05\,\Omega$, $R_1=0.1\,\Omega$, $C_{\mathrm{ser}}=10$ F, and $C_1=0.01$ F. The range of frequencies f is from 0.1 Hz to 100 kHz, where $\omega=2\pi f$.

Usually, a logarithmic distribution of frequencies is used to give enough points to cover different processes that might be far apart in terms of the direct frequency range.

It can be seen that R_{ser} is causing the high frequency portion of the spectrum (on the left) to intercept with X-axis at $0.05\,\Omega$, where imaginary portion becomes zero. Parallel R_1 and C_1 are causing the semicircle, whose right side again approaches zero imaginary part at lower frequencies with real value close to $R_{\mathrm{ser}}+R_1$. Finally, the curve goes vertical due to the serial capacitance C_{ser} that is very large and, therefore, shows a noticeable effect only at low frequencies (right of the graph). Note that such simple considerations allow to estimate the values of circuit elements from just looking at the Nyquist plot. However, that is not always possible for more complex circuits where time constants of different elements can overlap. This topic is discussed in the data analysis section.

Applications of Impedance Spectroscopy to Electrochemical Systems

Electrochemical processes are in general nonlinear, which means they cannot be described by linear differential equations or expressed as electric elements like resistors, capacitors, and inductors. Nonlinear systems cannot be solved by Laplace transformation and the concept of impedance is generally not well defined for them.

In spite of this limitation, all merits of the abovementioned formalism can still be applied to electrochemical system *provided* that voltage changes during electrochemical processes are small. Analysis of the Butler–Volmer equation that is central in electrochemical kinetics shows that at voltage changes below the thermal voltage value k_BT/e (about 25 mV at room temperature), the relation between current and voltage is linear. Therefore, analysis of electrochemical processes at small voltage changes can be replaced by analysis of equivalent electric elements. In particular, the relationship between voltage and current for simple electrochemical charge-transfer reaction becomes similar to Ohm's law, where the resistive element that corresponds to charge transfer is known as "charge-transfer resistance."

Other processes important in electrochemistry such as concentration polarization in adsorption and diffusion processes can be approximated through combinations of capacitors and resistors. Finally, electrochemical systems can exhibit actual physical capacitance across some films deposited at the electrodes and resistances (such as electronic and ionic resistance of porous electrodes). An overview of most of the important electrochemical processes that can be analyzed by impedance spectroscopy is given in subsequent sections. Furthermore, the Macdonald website (Macdonald, 2011) contains an extensive list of references dealing with complex nonlinear least squares (CNLS) analyses of a wide variety of solid and liquid materials; see the downloadable guide to electrochemically oriented publications listed there.

In addition to linearity conditions assured by small voltage excitation, several other requirements are needed to be preserved during an experiment in order to satisfy the assumptions of impedance spectroscopy. They include the following.

1. "Steady-state" requirement, which means that the system should not change during the measurement. For example if the system under test is a battery, its state of charge should not change during test, a result that can only be achieved if there is no bias current flowing between the electrodes that is not caused by a small excitation. Also, there should not be any other changes that can affect system response, such as change of temperature, pressure, and so on.
2. "Causality" means that the response should be reflecting only the excitation and no other effect, such as memory effects, from some prior measurements.

   Satisfying all the conditions can be checked by the absence of any additional frequencies of response sine waves except those of the excitation sine waves. This will be discussed in the measurement section.

PRACTICAL ASPECTS OF THE METHOD AND METHOD AUTOMATION

Basics of Measurement Apparatus

Impedance spectrum can be measured by modulating the voltage or the current signal and measuring voltage or current response, correspondingly. The device used for modulating voltage signal is called a "potentiostat" and for modulating current signal is called a "galvanostat." In most cases, electrochemical systems have their own potential between the electrodes, so it is very rare that voltage excitation is overlaid over a zero voltage difference.

Potential between electrodes reflects the state of electrochemical system; therefore, it is convenient to enforce certain potential that activates a process of interest. To isolate effects on just one electrode, typically a three-electrode configuration is used, where potential between electrode of interest (working electrode) and reference electrode is measured. Reference electrode potential difference from standard $H+H_2$ electrode is known beforehand, which allows to compare the potential of working electrode with the standard half-cell potentials available in reference literature for various electrochemical redox couples.

For example, to observe process of metal dissolution, potential needs to be set in the range close to the equilibrium potential E_{eq} of $\mathrm{Me}/\mathrm{Me}^{n+}$ couple, otherwise process would be too slow to be noticeable (impedance will be close to infinite). Equilibrium potential E_{eq} can be found from standard half-cell oxidation potential E_0 given known concentrations of active species as defined by Nernst equation (Equation 18).

Typically, potentiostats are capable to provide both the constant "bias" potential (e.g., 1.6 V) between the working and reference electrodes and variable voltage excitation of ±25 mV. Ideally, the current caused by bias potential should be low so that the system does not changes fast enough to have different parameters over the duration of impedance spectra measurement. For example, if there is an active corrosion current, surface area could change enough to cause different effective charge-transfer resistance. To achieve small currents, bias potential can be set at E_{eq} and then slowly ramped up until noticeable current starts. In galvanostatically controlled experiment, bias current can be set, which eliminates the need of searching for optimal potential. However, there is an additional caveat, since excitation is done by variable current, voltage response might turn out to be outside of linearity rage of less than 25 mV, so variable excitation level needs to be adjusted.

Overview of Available Measurement Systems

Although we have seen in the section "Principles of the Method" how to obtain impedance values from comparing magnitude and phase of excitation versus response sine waves, currently it is more common for electrochemists to use automated measurement systems. The most common system includes a signal generator to generate a sine-wave excitation of a required frequency, a potentiostat or a galvanostat, that amplifies the signal and forces the required voltage or current across a measurement system, and an analyzer that obtains phase and magnitude signal of a resulting response.

Such systems are widely commercially available. The field is dominated by Solartron Analytical with their "frequency response analyzer" (FRA) combined with a potentiostat. Control software allows one to make a scan of multiple frequencies to obtain a spectrum. The details of their system can be seen at http://www.solartronanalytical.com/Pages/1260AFRAPage.htm (Solartron Analytical). Other competing systems providers include Novocontrol, Hewlett Packard/Agilent, Gamry Instruments, Ametek Princeton Applied Research, Autolab, and ZAHNER-Elektrik.

FRA-based spectrometers provide high-quality impedance spectra but share common disadvantages, such as the requirement for a complicated signal generator or phase-sensitive detector and long measurement times for exploring a wide frequency range. The latter occurs because the impedance at each frequency is measured sequentially and the excitation for each frequency should be applied at least for two periods to prevent transient effects.

Accordingly, the time increase for the sequential measurement is excessively large if low-frequency data need to be measured. A method using a perturbation signal consisting of multiple sine waves and analysis of the response by fast Fourier transformation (FFT), which removes the necessity for a phase sensitive detector and allows a faster measurement, has been proposed in Popkirov and Schindler (1992). With this method, impedance data at many different frequencies can be obtained simultaneously. Therefore, the total measurement time is equal to the time required for the lowest frequency measurement. This approach also allows one to check for the absence of "additional" frequencies in the response spectrum, whose presence would indicate nonlinearity or nonstationary behavior of the system under test.

Another approach suitable for "self-made" systems due to its simplicity, that is based on Laplace transformation and does not require a frequency generator because a simple pulse excitation can be used, is described in Barsukov et al. (2002).

Impedance Spectra Analysis Systems

It is important to understand that there is no fully automatic way to obtain system parameters from impedance spectrum, with the exception of some most simple systems such as electric conductivity measurement of a block of conducting material. Even when using a commercially available impedance spectrum analysis software, it is necessary to understand the basic principles of impedance spectra analysis that is outlined in the next section. Given such familiarity, it is possible to shorten the development time by using commercial or public domain programs rather than developing your own. Most commercial programs are based on the open-source code in LEVM (Macdonald and Potter, 1987). Popular programs include Scribner's ZView, EChem Software ZSimWin, Dr. Boukamp's Equivalent Circuit, and Kumho's MEISP (MEISP, 2002).

DATA ANALYSIS AND INITIAL INTERPRETATION

Obtaining Model Parameters from the Impedance Spectrum

Let us consider the simplest case where the structure of the circuit is known but the values of the elements are unknown. How can we find the values given the impedance spectrum measured at the circuit terminals? Before attempting to find parameters, we have to ensure that the impedance spectrum was taken in a frequency range that makes all the circuit elements "visible" on the spectrum, for example, their impedances are not negligible.

This is a very important requirement since large capacitors, for example, would not appear in the high-frequency spectrum because their impedance values would fall below the noise level. Consider Figure 3. If we would have measured the impedance spectrum only until the frequency before the vertical line starts, we would not even know that capacitor C_{ser} existed, and certainly we would not be able to obtain its value from the fit. If we measured at frequencies above 100 kHz, we would not see any circuit elements except R_{ser}, because the impedance would show only a real part and look like a "dot" on the X-axis of the Nyquist plot at 0.05 Ω. For parallel RC elements, it is useful to know approximately what time constant, $\tau = \mathrm{RC}$, is expected for it, and make sure that the $1/\tau$ is within the frequency range of the experiment. In the case of physical systems, it is usually known from prior art in what frequency range a process is to be expected to appear; for example, a charge-transfer reaction or electrochemical double-layer RC element is typically between 1 kHz and 0.1 Hz and diffusion effects often appear below 0.1 Hz. Examples of typical frequency ranges are given in Appendix II discussing distributed elements.

Once it is assured that the spectrum actually contains information about the parameters, this problem can be considered as a parameter optimization problem in the form

$$Z = f_Z(\omega, P) \tag{10}$$

where Z is a vector of complex impedance values that corresponds to circular frequency values in vector ω, f_Z is the complex function of circular frequency (e.g., the function $Z(i\omega)$ detailed in Equation 8), and P is a vector of function parameters to be optimized. Typically, such optimization problems can be solved using a suitable nonlinear least-square fit algorithm. Most popular is the Levenberg–Marquardt algorithm. Care should be taken while using a version of the algorithm that supports complex function values, the CNLS approach. Many mathematical packages such as Mathcad or Mathematica support such complex optimization. There are also stand-alone programs specially developed for immittance (either impedance or admittance) data fitting such as LEVM (Macdonald and Potter, 1987).

Unfortunately, nonlinear fitting is, in general, an ill-posed problem and is not guaranteed to converge to the global minimum or to converge at all. Convergence is largely dependent on the closeness of the parameter initial guesses to final values. Some other optimization choices such as weighing of outliers and different criteria for optimization also affect convergence. For details on such choices, refer to Macdonald et al. (1982). Meanwhile, let us consider some ways to find a good initial guess.

Manually, such a search would be similar to parameter estimation from Nyquist plots, as demonstrated, for example, in Figure 3. Serial resistance can be estimated from the real part of the "left," high-frequency edge of the spectrum, while "width" of each semicircle gives an estimate for resistor values associated with that particular RC couple. The sum of all resistors in the circuit usually adds up to the real part of the low-frequency edge. Once resistor values are estimated, capacitor values can be found by taking the points in the middle of corresponding semicircles and finding which frequency f_{mid} corresponds to these points. The time constant τ of the RC couple will be $\tau = 1/f_{\mathrm{mid}}$, and from it, C can be estimated as $C = \tau/R$.

For simpler circuits that consist of just multiple RC couples connected in series, this finding of initial guesses can be automated. After substitution of $C = \tau/R$ into the impedance equation for an RC couple, we get an equation that is linear with respect to R:

$$Z(\omega) = 1/(1/R + i\omega C) = R(1/(1 + i\omega\tau)) \qquad (11)$$

Optimization of a sum of any number of linear equations is a linear regression problem that is guaranteed to converge. This allows us to assign fixed values of $\tau_{[\mathrm{index}]}$ that are logarithmically distributed along the frequency range of the spectrum, and find an estimate of $R_{[\mathrm{index}]}$ for each RC couple by linear regression. After that, a nonlinear fit, where both R and τ are free, may be performed to find final values.

An automatic analysis that attempts to find the number and values of RC elements that can represent particular impedance spectrum is useful if a circuit for the system under test is unknown. In this case, we could start, for example, with 10 RC elements and keep reducing them until the sum of least square errors starts increasing. The final number of RC elements and their values gives an indication of how many distinct processes are responsible for this impedance spectrum. Such "distribution of relaxation times" analysis can be done automatically in LEVM. An alternative method of preliminary analysis of a spectrum of unknown system known as "differential impedance analysis" is described in Vladikova (2004).

A variation of the RC element-finding method can be performed to find raw initial guesses not only for circuits that do not consist of multiple RC elements but also for elements that can be associated with time constants. Resulting values of RC time constants can be assigned to time constants of actual circuit elements that give a good initial guess for the nonlinear fit of the actual system.

Such an approach also allows reducing the ambiguity of the results of the fit. For example, it is known that a diffusion time constant should be lower than that of a charge-transfer reaction. Assigning an initial guess from the "low-frequency" RC element to a diffusion element and that from high-frequency RC element to a charge-transfer resistance or double-layer couple will force the choices to be in the right frequency ranges. Note that a nonlinear fit itself is oblivious to the physical meaning of particular elements of the circuit and thus it might not produce parameters that would make diffusion with a smaller time constant than charge transfer, unless "pushed" in right direction by assigning initial guesses. Automatic initial guess finding with time constant order assignment is implemented in MEISP (MEISP, 2002).

After optimization is performed, it is important to verify that a fit reflects all features of the spectrum, for example, no semicircle visible in the spectrum is "ignored" by the fit line or two semicircles are not described with just one by the fit. Other features such as a 45° line or depressed semicircle that we will discuss later should also be correctly represented. A plot of residuals (differences between fit and actual data) should look "randomly distributed" if fit is correctly describing all features of the spectrum, and not have biases such as systematic errors in either direction. This is, unfortunately, an ideal not actually fully achieved in most fitting of models to data sets. There is usually a trade-off between model complexity and the degree of reduction of systematic errors.

It is also important to verify that time constants for all the processes have their expected position with respect to each other, as discussed previously.

Discrete Elements

Many common electrochemical processes can be represented as discrete "equivalent" elements with analytical solutions for their impedance versus frequency equations. Refer to Appendix I for a collection of frequently used discrete elements. All equations are given for a unit area of electrode surface except where noted otherwise, so electric parameter units would be $i = \mathrm{A/cm^2}$, $R = \Omega\ \mathrm{cm^2}$, and $C = \mathrm{F/cm^2}$.

Distributed Elements

Many electrochemical processes do not correspond to simple elements such as resistors and capacitors because they are described by differential equation involving partial derivatives (e.g., diffusion or distribution of activation energies in the solid). However, they do satisfy all the linearity conditions required to apply the impedance spectroscopy approach, and impedance equations can be derived for these processes by applying the Laplace transform to the governing equations (see, e.g., Barsukov and Macdonald, 2005, Chapter 2.1.3).

Such processes can be still used as elements of an equivalent circuit along with resistors and capacitors, since their impedance follows the same "additive" rule for serial connection. Some of these processes can be represented by simple electrical circuits, but those of more complex nature, such as diffusion, cannot be represented with finite number of discrete elements (although it can be represented as an infinitely repeated chain-connected resistor or capacitor network, in electronics, known as a "transmission line"). They are commonly called "distributed" circuit elements. Appendix II includes a collection of commonly used distributed elements. Some others are included for use as parts of fitting models in the LEVM computer program and are listed in its extensive manual (Macdonald and Potter, 1987; Macdonald website, 2011).

Some Common Models for Fitting Impedance Spectroscopy Data

Although nearly all impedance spectroscopy data sets involve some constant phase element (CPE) power-law behavior at low, high, or both frequency regions, such data generally include more than one dispersive process and several time constants. Analysis and fitting models more complex than a CPE function or a single transmission line are thus frequently required. Since Maxwell's equations show that it is impossible to distinguish between displacement and conduction currents by electrical measurements alone (Macdonald et al., 1999; Macdonald, 2008), one must usually invoke other knowledge about the system when attempting to choose an appropriate model and apply it at either the impedance or the dielectric immittance level. Therefore, when models may be readily expressed in algebraic form, here we shall express them in terms of a general $I(\omega)$ immittance function that can be applied at either level. The result can thus describe either conductive-system or dielectric-system relaxation/dispersion.

1. An iconic, widely used empirical model is the Havriliac–Negami, which, along with its simplifications, is described, e.g., in Macdonald (2010). It may be written as

$$\frac{I_{k(\omega)}}{I_{k(0)}} = \frac{1}{[1+(i\omega\tau)^{\alpha}]^{\gamma}} \tag{12}$$

   Here τ is a characteristic relaxation time, and α and γ usually fall in the range from zero to unity. For impedance response, the subscript symbol $k=0$ and $I_0(0) \equiv Z'(0) \equiv R_0$, while for dielectric-level response $k=D$; therefore, it is customary to write $I_D(\omega) \equiv \varepsilon_D(\omega) = \varepsilon_\infty + \Delta\varepsilon/[1+(i\omega\tau)^{\alpha}]^{\gamma}$, where $\Delta\varepsilon \equiv \varepsilon_0 - \varepsilon_\infty$ and ε_∞ is the high-frequency-limiting dielectric constant. The Havriliak–Negami model thus potentially involves four or five free parameters.

   Note that when the values of α and γ are both fixed at unity, Equation 11 reduces to single-time-constant Debye response at either the impedance or the dielectric permittivity level. Alternatively, when $\gamma=1$, it reduces to Cole–Cole response, widely used for analysis of liquid electrolyte data. Unfortunately, the $k=0$ responses of both the general Havriliak–Negami model and that of the Cole–Cole response do not reduce to a physically correct low-frequency-limiting power law with an exponent of two for the real part of the admittance in this limit. This defect is not present, however, for the Davidson–Cole model defined for $\alpha=1$. Furthermore, the Davidson–Cole model is less empirical than the other two and may even be derived from fractal considerations. Even though the Havriliak–Negami model with its extra free parameters may frequently be found to fit data better than the Davidson–Cole model, the latter is more realistic and should be preferred for both fitting and interpreting data, especially when an impedance model is appropriate.

2. Although many models are only available for fitting in numerical form, an early physically plausible model that can be expressed algebraically is the Poisson–Nernst–Planck (PNP) effective medium for ordinary diffusion of positive and negative mobile charges of arbitrary mobility in the material of a finite-length cell with fully blocking electrodes (Macdonald, 1953; Macdonald and Franceschetti, 1978): its anomalous-diffusion version, the PNPA (Macdonald, 2010; Macdonald et al., 2011), and the partially blocking PNP/PNPA model (Macdonald, 2011). For these models Poisson's equation is satisfied throughout. The fully blocking PNPA expression (Macdonald et al., 2011) (Equation 6) may be written for full or small charge dissociation as

$$Z_a = R_\infty \frac{(i\omega\tau)^{\gamma} + \dfrac{\tanh(Mq_a)}{Mq_a}}{(i\omega\tau)^{\gamma}(1+i\omega\tau) + [i\omega\tau - (i\omega\tau)^{\gamma}]\dfrac{\tanh(Mq_a)}{Mq_a}}$$

   where $R_\infty \equiv 1/G_\infty$, G_∞ is the high–frequency-limiting conductance, $\tau \equiv R_\infty C_\infty$, C_∞ is the high-frequency-limiting bulk capacitance, $M \equiv L/2L_D$, the number of Debye lengths in half the cell length, $q_a = [1+(i\omega\tau)^{\gamma}]^{1/2}$, and $0 < \gamma \le 1$. When $\gamma = 1$, the result is PNP response that is found to be closely equal to dielectric-level dipolar Debye behavior when $M \ge 1$, even though the conduction process here involves mobile charges (Macdonald, 2010). When $\gamma < 1$, however, the PNPA anomalous diffusion case, this model has been shown to well fit experimental data sets of several disparate ionically and electronically conducting materials (Macdonald, 2011; Macdonald et al., 2011) and involves CPE-like behavior at low frequencies. Furthermore, in its LEVM instantiation (Macdonald website, 2011) it includes arbitrary mobilities of the two charge types, the possibility of their generation recombination from neutral centers, and can account for full or partial blocking of charges at the electrodes, as well as possible specific adsorption (Macdonald and Franceschetti, 1978). In addition, it can lead to estimates of both the original neutral-center concentration as well as those of the dissociated charges, particularly important for the usual case in solid materials of small dissociation (Macdonald, 2011).

3. Several interesting conductive-system impedance-spectroscopy data analysis models, referenced in the Macdonald website Guide mentioned in the section "Applications of Impedance Spectroscopy to Electrochemical Systems," are only available in numerical form for fitting data. A particularly valuable one, instantiated in the LEVM computer program, is the Kohlrausch CK1 model, whose strengths and relevant references are summarized in a section of the Macdonald website. Its K1 part dates since 1973 and has been derived from both macro and microscopic analyses with the latter showing that it is a continuous-time, random-walk hopping model.

In the time domain, it has frequently been found, since the work of Kohlrausch in the 19th century, that the discharge current of a fully charged material containing mobile charges decays as a stretched exponential of the form $\phi(t) \propto \exp[-(t/t_0)^{\beta}$ with $0 < \beta \leq 1$, stretched when $\beta < 1$ In the stretched case, the one-sided Fourier transform to the frequency domain must be carried out numerically that directly leads to what has been called the K0 model, whose high-frequency capacitance approaches zero, thus requiring the addition of a parallel capacitance representing ε_∞ and leading to the CK0 model.

Interestingly, the K1 model, also derived from stretched exponential temporal response and expressed at the electric modulus level (Macdonald, 2009), leads to a constant capacitance in the high-frequency region, wrongly identified in the earlier work as ε_∞ Thus, the full fitting model must also include a parallel capacitance and is termed the CK1. It has been found to well-fit conductive-system data sets for many different materials with a value of β very close to one third and independent of the temperature and ionic concentration! In this case, it is named the CUN, with UN standing for "universal" (probably an exaggeration), and it then involves only three free parameters. Nevertheless, when fitting impedance spectroscopy data in either the time or the frequency domain, it is important to fit with several different models to find the most appropriate one.

Example of Impedance Spectrum Analysis for Bithiophene Electropolymerization

This section gives an example of impedance spectra and its analysis. Data used for this section were recorded during electropolymerization of bithiophene resulting in the formation of a thin electrically conductive polybithiophene layer. The test setup is the same as described in the section "Sample Preparation." A Nyquist plot of the data is shown in Figure 4.

This data has been published earlier in Barsukov (1996, Chapter 4.3, Fig. 32 (0.1 s)). However, the analysis given here uses a simplified model that focuses on the most pronounced electrochemical processes.

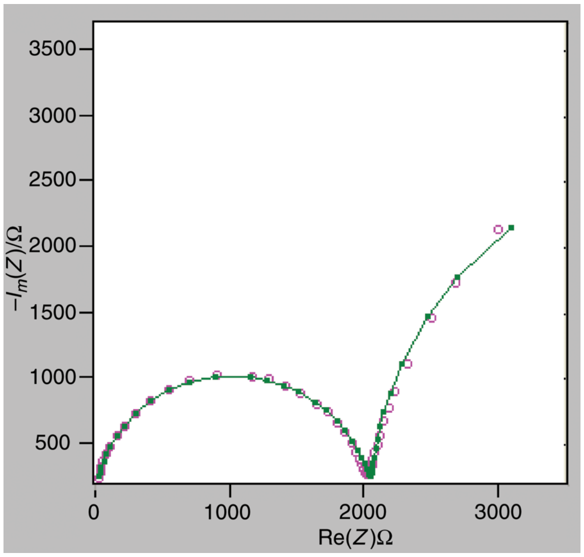

Figure 4. Nyquist plot of impedance spectrum of a thin polybithiophene film during electropolymerization of bithiophene. Circles are raw data and the line is the model fit.

The analysis of impedance spectroscopy mostly follows five steps.

1. ***Understanding the System***: In this case, the system includes two processes. The first process is due to a highly conductive polybithiophene film deposited on the electrode surface. Polybithiophene undergoes an oxidation/reduction reaction if the applied voltage is varied, with subsequent diffusion of the counter-ions that compensate the injected charge into the bulk of the film. Since the film is thin (polymerization is at early stages), the diffusion is limited by the thickness of the film. Conductivity of the film is very high so its resistance can be neglected.

   The second process is a polymerization of bithiophene. It is limited by its charge-transfer resistance. Bithiophene also diffuses from the bulk of the electrolyte but due to the small electrode size and excess of bithiophene monomer, this is not a limiting step.
2. ***Devising a Model***: Charge-transfer resistance due to oxidation/reduction of the polymer would be in series with the finite-length diffusion element and both of these components would be in parallel with the electrochemical double layer. Polymerization reaction is not limited by diffusion in the polymer, and will therefore appear as independent charge-transfer resistance in parallel to all these components. There is also a serial resistance that is always present due to ohmic resistance of the electrodes and wires as well as small portion of electrolyte between the tip of the Luggin capillary tube that connects reference electrode and the cell and the working electrode. Such model can be represented as an equivalent circuit in Figure 5.

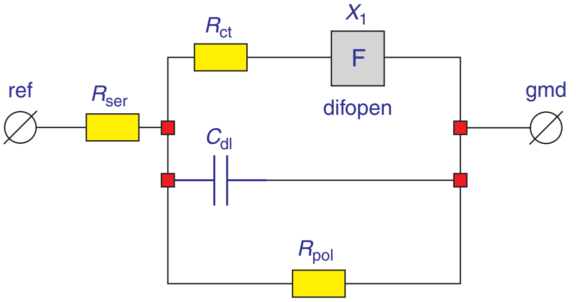

Figure 5. Equivalent circuit of polybithiophene/electrolyte system in the presence of a polymerization reaction. Here, R_{ser} is the serial resistance and R_{ct} is the charge-transfer resistance of polybithiophene redox reaction, X_1 is a distributed element representing limited length diffusion with a blocking boundary, C_{dl} is the double layer capacitance, and R_{pol} is the charge-transfer resistance of the bithiophene polymerization reaction.

3. ***Deriving the Impedance Equations for the Model***: The impedance equation for the model in Figure 5 can be derived using the simple rule that serially connected impedances add up and parallelly connected admittances (an inverse of impedance) add. This way we start with R_{ser} that gives us

   $Z(\omega) = R_{\text{ser}} + Z_{\text{cir1}}$, where Z_{cir1} includes everything else, and ω is the circular frequency, related to the usual frequency $f = \omega/2\pi$. Note that most commercial impedance spectrometers would store usual frequency "f" unless specified, so you would need to convert it to ω to use the above equations.

   Now we have three components that are in parallel in the remaining circuit: R_{pol}, C_{dl}, and R_{ct} serially to X_1. First, let us calculate impedances of these components. They are R_{pol}, $1/(C_{\text{dl}} i\omega)$, and $R_{ct} + Z_{X_1}(\omega)$. Now to use the admittance addition rule, we turn these values into admittances as $Y = 1/Z$. This gives us $1/R_{\text{pol}}$, $C_{\text{dl}} i\omega$, and $1/[R_{ct} + Z_{X_1}(\omega)]$.

   The admittance of the total circuit will be the sum of parallel element admittances, for example,

$$Y_{\text{cir1}} = \frac{1}{R_{\text{pol}}} + C_{\text{dl}} i\omega + \frac{1}{[R_{\text{ct}} + Z_{X_1}(\omega)]}$$

Now to get the impedance of the circuit, we use $Z = 1/Y$ to get

$$Z_{\text{cir1}} = \frac{1}{\{1/R_{\text{pol}} + C_{\text{dl}} i\omega + 1/[R_{\text{ct}} + Z_{X_1}(\omega)]\}}$$

Substituting it into equation for the total impedance $Z(\omega)$ we get

$$Z(\omega) = R_{\text{ser}} + \frac{1}{\{1/R_{\text{pol}} + C_{\text{dl}} i\omega + 1/[R_{\text{ct}} + Z_{X_1}(\omega)]\}}$$

One missing impedance function is $Z_{X_1}(\omega)$—reflective finite-length Warburg impedance. This impedance function was first used in electrochemistry by Ho et al. (1980), and it is described in more detail in Appendix II, Equation 21. Substituting this function into Equation 21 and substituting $s = i\omega$ we get

$$Z(\omega) = R_{\text{ser}} + \cfrac{1}{\cfrac{1}{R_{\text{pol}}} + C_{\text{dl}} i\omega + \cfrac{1}{R_{\text{ct}} + \sqrt{\cfrac{R_d}{C_{\text{d}} i\omega}} \coth(\sqrt{R_d C_{\text{d}} i\omega})}} \tag{13}$$

4. ***Fitting the Data to Optimize the Model Parameters***:
   To simplify this example, we can use the trial version of MEISP impedance analysis software (MEISP, 2002) (which is a front-end to LEVM) to fit this data by optimizing parameters R_{ser}, R_{pol}, C_{dl}, R_{ct}, R_{d}, and C_{d}. It allows one to make a circuit, as in Figure 5, using a built-in circuit editor and to use a ready-made function for $Z_{X_1}(\omega)$ (reflective finite-length Warburg impedance). Normally, you would also need to come up with an initial guess for the values, but MEISP has a "pre-fit" option where it finds initial guess values by roughly mapping time constants of the analyzed circuit to that of a series of RC elements.

   Time-constant order has to be specified according to the prior knowledge of the system. R_{ser} is always the highest frequency (so order 0), whereas, otherwise, the typically highest frequency RC element corresponds to R_{ct} and C_{dl} (so order 1). Then come the polymerization reaction (order 2) and diffusion components R_{d} and C_{d} involving lowest frequency response (order 3).

   The resulting fit curve is shown as a continuous line in Figure 4 and the parameters and their estimated standard deviations are given in Table 1.

   It is important to evaluate the fit accuracy and parameter confidence levels. In this case, the fit is visually good (more detailed analysis would include looking at the distribution of residuals). R_{ser} was not determined with good confidence because of its extremely low value (value 1 for relative standard deviation means "singular matrix"). Confidence intervals obtained for other parameters are below 0.2, which means that physical processes are sufficiently prominently

Table 1. Optimized Parameter Values and Relative Standard Deviations Obtained During Fitting the Spectrum of Figure 4 with the Function in Equation 13

Parameter	Value	Relative Standard Deviation
R_{ser}	3.1210e−004 Ω	1
R_{ct}	2.7379e+003 Ω	6.7e-03
C_{dl}	4.3673e−008 F	2.5e-03
R_d	3.9333e+002 Ω	1.0e-01
C_d	6.7774e−006 F	1.3e-02
R_{pol}	7.4008e+003 Ω	1.4e-02

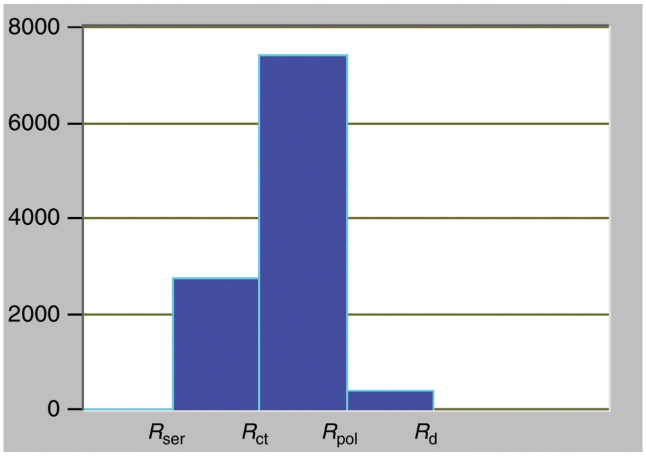

Figure 6. Relative contributions to total Re(*Z*) by different processes.

represented by this impedance spectrum. The worst value here is for R_d (0.1); it is larger than values for other parameters because of the small value of R_d. By plotting the values of all resistive components as in Figure 6, it can be seen that R_d is much smaller than other values.

5. ***Using the Parameters to Find Physical Properties***:

The relative reaction rates of redox reaction and polymerization may be compared by just looking at the values of R_{ct} and R_{pol}. Clearly, the polymerization reaction has a smaller rate constant since they both take place on the same surface. To compare with other experiments, charge-transfer resistances are usually expressed in area-independent form $R_{ct} = R_{ct}/S$, where S is the electrode area. In this case, it is known from the diameter $d = 0.5$ mm of the platinum disc used as electrode (see Section "Sample Preparation" for details). This gives us $S = \pi d^2/4 = 1.967\text{e-}07\ \text{m}^2$ and relative charge-transfer resistances of $R_{ct} = 1.39\text{e}010\,\Omega/\text{m}^2$ and $R_{pol} = 3.769\text{e}010\,\Omega/\text{m}^2$.

In this case, quantitative values of the rate constant can also be found. The relationship between the charge-transfer resistance and the rate constant is given in Equation 19 in Appendix I. It requires, however, some additional values not usually available from impedance experiments, such as the standard half-cell potential of the oxidation reaction, E_0, and the concentration of the reduced and oxidized species c_{tot}. E_0 can be found using cyclic voltammetry method (see article CYCLIC VOLTAMMETRY).

The voltage effect of concentration change, dE/dc, may be found from C_d, as given in the description of the "reflective finite-length Warburg" element in Appendix II, if the diffusion length "*d*" (in this case thickness of the polymer layer) is known:

$$\frac{dE}{dc} = \frac{FndS}{C_d}$$

Here n is number of electrons participating in reaction, in this case 1.

From polymer density and amount of polymer considerations, d has been estimated for this case in Barsukov (1996) as 80 nm.

On substituting the values of C_d and d, we get $dE/dc = 2.236\text{e-}04\ \text{V m}^3/\text{mol}$.

The diffusion constant D can be found from R_d and C_d values, given a value of the diffusion length d, as

$$D = \frac{d^2}{C_d R_d}$$

On substituting the values from Table 1, we get

$$D = 2.4\text{e}{-}012\ \text{m}^2/\text{s}.$$

SAMPLE PREPARATION

While studying the electrochemistry of liquids, it is common to investigate the behavior of an electrochemical reaction on just one of the electrodes by subtracting the effect of other components of the cell. This is done by comparing the potential at the "working" electrode under test with the electrochemical potential of a passive "reference" electrode close to its surface with a potentiometer with high-ohmic input. Since only negligible current is flowing between the working and the reference electrodes due to the voltage measurement, the impedance of the reference electrode itself does not matter.

At the same time, the excitation signal is applied between the "working" and the other much larger "counter" electrode located in the bulk of the cell and sized to minimize its impedance and to provide a homogeneous field around the working electrode. Since measurements are made only between the reference and the working electrode, the impedance of the "counter" electrode, as well as that of the electrolyte between the working and the counter electrodes, is also excluded. Here, the electrolyte should be highly ionically conductive to avoid any local potential gradients, so typically a salt that is passive in the potential window under investigation, such as $LiClO_4$, is added to the solvent in large amounts (typically, 1M or more).

An example of such a three-electrode cell is shown in the Figure 7.

The working electrode used for investigation can be made by inserting a platinum wire into a glass capillary, melting the capillary so that the wire is imbedded in the glass, cutting the left-over wire, and polishing the glass/platinum composite perpendicular to the cut until the platinum surface is coplanar with the flat glass surface. The platinum disk is exposed to the electrolyte and constitutes a mini electrode whose diameter is precisely controlled by the diameter of the original platinum wire. In the experiment described in the section "Example of Impedance Spectrum Analysis for Bithiophene Electropolymerization," a 0.5-mm diameter wire was used.

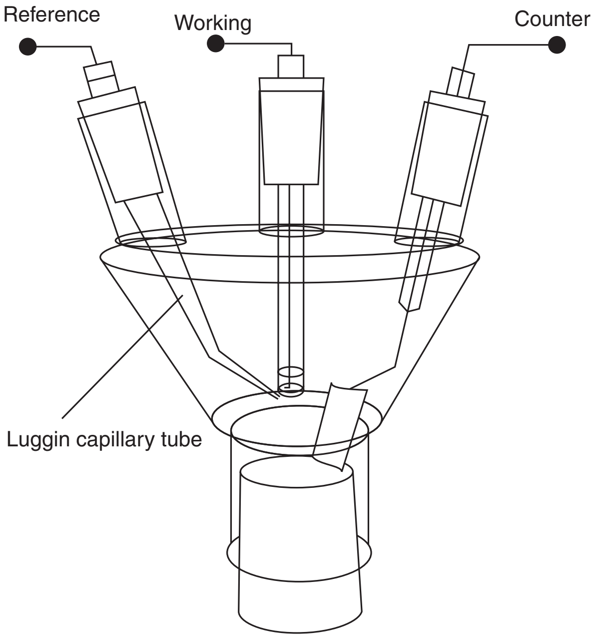

Figure 7. Three-electrode cell used for electrochemical measurements.

This cell is suitable for measurement of the impedance of the processes on the working electrode. However, some unusual considerations apply to a reference electrode to be used for impedance measurement as compared to traditionally used references. Because distortions in the case of AC measurement can be both resistive and capacitive, it is important that the electrode itself, as well as the Luggin capillary tube filled with electrolyte, does not have an impedance too large so that the impedance remains less than that of the electrometer. This is more difficult to achieve for organic electrolytes, required for many systems commonly investigated. A good reference electrode for impedance measurement in organic electrolyte is a silver wire in a solution of its own salt. Details on a typical setup of electrochemical impedance measurement can be found in Barsukov (1996).

PROBLEMS

Most problems are related to attempts that apply the method to systems that do not completely satisfy some of the impedance concept requirements, in particular, linearity, steady state, and causality.

The linearity requirement would be violated if the process in question cannot be described by an ordinary differential equation. In electrochemistry, it would be, for example, a current/voltage relationship whose voltage deviation is much larger than 25 mV. In this case, the full Butler–Volmer equation (Equation 14) should be used to describe the relationship rather than the linearized form that is similar to Ohm's law. The impedance concept no longer applies to such systems. If you apply a single sine-wave excitation and make an FFT from the response, you will observe multiple additional frequencies instead of a single-response frequency. Such "frequency splitting" is a sign that some of the requirements of impedance spectroscopy are violated, although it requires a complex additional analysis to find which one.

The simple approach is to try eliminating one of the three possible suspects and retest until frequency splitting disappears. For example, reducing the magnitude of the excitation current can reduce voltage response to below 25 mV, thus eliminating nonlinearity. Making sure that all chemical (e.g., change of state of charge) or physical processes caused by temperature change are completed prior to measurement by adding relaxation time can ensure the steady-state condition. Eliminating additional factors during the experiment can assure the causality requirement. Note that for all of this analysis, it is beneficial to have the ability to analyze the response signal in greater detail (FFT) than many of the commercial FRA allow. The ability of multifrequency analysis could thus be one of the criteria in choosing or designing an impedance measurement apparatus.

Another common problem especially for low-frequency impedance measurement is that the sine wave might not be applied for sufficient intervals before the measurement is done. First, sine-wave response includes a transient component due to the load onset, while sine-wave analysis assumes that sine waves were applied long enough so that the initial transients are completely dissipated. This effect also causes a multi-frequency response that is seen as multiple frequencies in the FFT spectrum. It can be simply fixed by adding at least one period delay after the sine-wave onset before the measurement, which unfortunately means a longer test time (e.g., for 1 mHz measurement, you will need to add 1000 s additional measurement time). Laplace transform measurement does not suffer from this problem because no assumption of absence of transient effect is made.

A most common problem in impedance analysis is that the same spectrum can fit perfectly with a variety of different equivalent circuits. For example, serially connected parallel RC elements and parallelly connected *R–C* serial chains would produce the same impedance spectrum if all *R* and *C* values were optimized. This makes it clear that a good fit of impedance spectrum by a particular circuit (or equation) does not prove that this circuit or equation is a good representation of the physical processes in the system. If a model is not physically relevant, a good fit will still produce completely meaningless parameter values. For this reason, it is critical to follow the steps from physical understanding of the system to model creation and only then followed by fitting the data, as exemplified in the section "Example of Impedance Spectrum Analysis for Bithiophene Electropolymerization."

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Macdonald, 2011. See above.

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Macdonald, J. R. website.

It includes a link (http://jrossmacdonald.com) to download the free newest WINDOWS version, LEVMW, of the comprehensive LEVM fitting and inversion program. The program includes an extensive manual and executable and full source code. Commercial programs derived from this open code include ZView and MEISP. All of the J. R. Macdonald papers cited herein are available in PDF format for downloading from the above link. Their numbers in the temporally ordered list in the website are shown as {xx} in the present citation list.

APPENDIX I: COMMONLY USED DISCRETE ELEMENTS

1. Current due to activated electron transfer when diffusion limitations are negligible.
   (a) ***Governing Equation (Butler–Volmer):***

$$I = Si_0\left[e^{\frac{(1-\alpha)nF}{RT}(E-E_{eq})} - e^{\frac{-\alpha nF}{RT}(E-E_{eq})}\right] \tag{14}$$

Here and below, "R" in thermodynamical equations, such as Equation 14, where it is multiplied by temperature T, denotes gas constant, 8.3144621 J/K/mol, and "F" denotes Faraday constant 96,485.3365 C/mol. In all "electrical" equations, R and F denote resistance (Ohm) and capacitance (Farad), respectively.

(b) ***Electrochemical Parameters:***
If n = number of electrons,
α (usually around 0.5) = transfer coefficient,
E = present potential at the electrode surface, and
S = surface area, then i_0 exchange current is given as

$$i_0 = n\mathrm{F}k_0 c_{\mathrm{ox}} \mathrm{e}^{\left[\frac{-\alpha n\mathrm{F}}{\mathrm{RT}}(E_{eq}-E_0)\right]} \tag{15}$$

where k_0 is the rate constant of the redox reaction.

(c) ***Small Voltage Equivalent Equation:*** $I = \Delta E/R_{\mathrm{ct}}$ (Ohm's law).
$\Delta E = E - E_{\mathrm{eq}}$ is overpotential and is the difference between the present and equilibrium potentials.

(d) ***Equivalent Electric Element:***
Charge-transfer resistance is given as

$$R_{\mathrm{ct}} = \frac{\mathrm{RT}}{n\mathrm{F}i_0} \tag{16}$$

It can also be expressed through concentration and rate constant by substituting the equation of exchange current i_0 given in Equation 15 as

$$R_{\mathrm{ct}} = \frac{\mathrm{RTe}^{\frac{-\mathrm{F}\alpha n(E_0-E_{\mathrm{eq}})}{\mathrm{RT}}}}{\mathrm{F}^2 k_0 n^2 c_{\mathrm{ox}}} \tag{17}$$

Here c_{ox} is the concentration of oxidized species, k_0 is the rate constant of the redox reaction, and E_0 is the standard half-cell oxidation potential.

The ratio between concentrations of oxidized and reduced forms of active species, c_{ox} and c_{red}, depends on the equilibrium potential E_{eq} as defined by Nernst equation:

$$E_{\mathrm{eq}} = E_0 + \frac{\mathrm{RT}}{n\mathrm{F}}\ln\left(\frac{c_{\mathrm{ox}}}{c_{\mathrm{red}}}\right) \tag{18}$$

Since both c_{ox} and E_{eq} in Equation 17 depend on the amount of charge passed through the electrochemical system before equilibrium was reached, they are both "state variables." To make just one state variable, c_{ox} in Equation 17 can be expressed by E_{eq} and c_{tot} (the sum of c_{ox} and c_{red}) using the Nernst equation. Since the sum of the concentrations c_{tot} remains constant and is a permanent system property, we are then left with just one state variable E_{eq} defining R_{ct} shown in Equation 19.

$$\mathrm{R}_{ct} = \frac{\mathrm{RTe}^{\frac{\mathrm{Fn}(\alpha-1)(E_0-E_{\mathrm{eq}})}{\mathrm{RT}}}\left[\mathrm{e}^{-\frac{\mathrm{Fn}(E_0-E_{\mathrm{eq}})}{\mathrm{RT}}}+1\right]}{C_{\mathrm{tot}}\mathrm{F}^2 n^2 k_0} \tag{19}$$

2. Double-layer capacitance.

(a) ***Governing Equation:***

$$I = C_{\mathrm{dl}}\mathrm{d}E/\mathrm{d}t \tag{20}$$

(b) ***Small-Voltage Approximation:***
Same.

3. Reaction of monolayer of active species adsorbed at smooth surface.

(a) ***Governing Equation:***

$$i = \frac{\mathrm{d}E}{\mathrm{d}t}\frac{\mathrm{F}n}{\mathrm{d}E/\mathrm{d}c} \tag{21}$$

Here, dE is the voltage deviation from steady-state voltage and dc is the surface concentration deviation from the equilibrium value.

dE/dc can be further determined if a process is exactly described by the Nernst equation (typically, for diluted solutions and low coverage levels of adsorbed species) as

$$\frac{\mathrm{d}E}{\mathrm{d}c} = \frac{\mathrm{RT}}{\mathrm{F}nc_{\mathrm{tot}}}\frac{\mathrm{e}^{\frac{n\mathrm{F}(E_{\mathrm{eq}}-E_0)}{\mathrm{RT}}}}{\left[\mathrm{e}^{\frac{n\mathrm{F}(E_{\mathrm{eq}}-E_0)}{\mathrm{RT}}}+1\right]^2} \tag{22}$$

Note that in cases of higher concentrations, Frumkin isotherm has to be used instead of Nernst equation. See Conway (1999) for detailed treatment of pseudocapacitance for various systems.

(b) ***Electrochemical Parameters:***
E_O = equilibrium potential of redox reaction,
E = applied electrochemical potential, and
$c_{\mathrm{tot}} = c_{\mathrm{ox}} + c_{\mathrm{red}}$ is the bulk concentration of active species (sum of oxidized and reduced-form concentrations).

(c) ***Small-Voltage Equivalent:***

$$I = C_{\mathrm{ps}} \cdot \mathrm{d}E/\mathrm{d}t \tag{23}$$

(d) ***Equivalent Electric Element:***
Pseudocapacitance of redox reaction of an active species adsorbed on the surface of an electrode in F/cm^2

$$C_{\mathrm{ps}} = \frac{\mathrm{F}n}{\mathrm{d}E/\mathrm{d}c}$$

In the case of Nernstian redox reactions, $\mathrm{d}E/\mathrm{d}c$ can be substituted from Equation 22 as

$$C_{\mathrm{ps}} = \frac{2\mathrm{F}^2 n^2 \left[\cosh\left(\frac{\mathrm{F}n(E_{\mathrm{eq}}-E_0)}{\mathrm{RT}}\right) + 1\right] c_{\mathrm{tot}}}{\mathrm{RT}} \qquad (24)$$

APPENDIX II: COMMONLY USED DISTRIBUTED ELEMENTS

1. ***Reaction of Mobile Active Species Distributed in Infinite Layer***:

Linear diffusion from a medium whose length can be approximated as infinite results in an impedance analogous to that of an infinite length transmission line composed of capacitors and resistors

$$Z(s) = \frac{\mathrm{d}E}{\mathrm{d}c}\frac{1}{n\mathrm{F}\sqrt{sD}} \qquad (25)$$

Here D is the diffusion coefficient of the reaction rate-limiting mobile species in the medium.

Governing equation in the Laplace domain: (infinite-length Warburg impedance)

$$I(s) = E(s)/Z(s) \qquad (26)$$

$\mathrm{d}E/\mathrm{d}c$ can be further determined for Nernstian reactions as in Equation 22.

- Typical shape in complex presentation is shown in Figure 8.
- Impedance function in terms of electric parameters:

$$Z(s) = \sqrt{\frac{R_{\mathrm{d}}}{sC_{\mathrm{d}}}} \qquad (27)$$

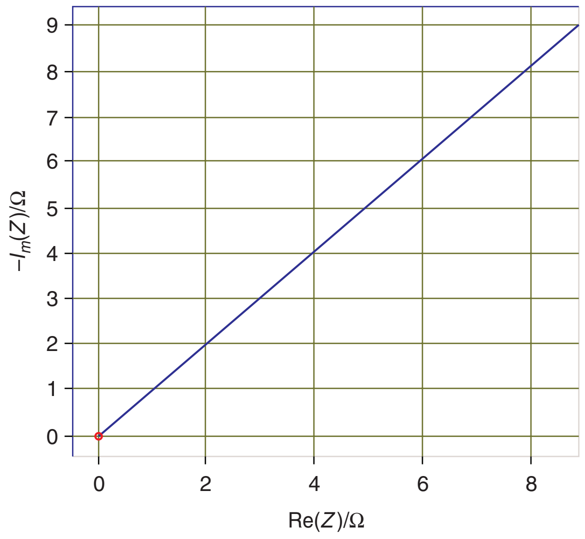

Figure 8. Impedance spectrum of diffusion with infinite boundary condition, $R_d = 1\ \Omega/\mathrm{cm}$, $C_d = 1\ \mathrm{F/cm}$, from 10 kHz to 1 mHz.

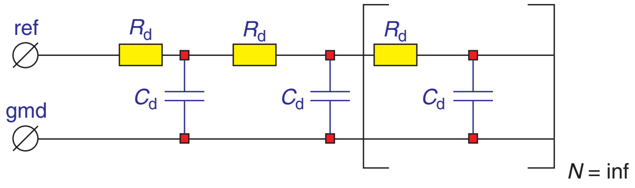

Figure 9. Equivalent circuit of an infinite boundary transmission line.

- Schematic presentation of the circuit illustrated in Figure 9.
- Fit parameters.
  C_{d} in F/cm
  R_{d} in Ω/cm
- Conversion into electrochemical parameters. Here S is the geometric electrode area in cm^2, n is the number of electrons participating in the reaction, and c is the volume concentration in $\mathrm{mol/cm}^3$.

$$\frac{\mathrm{d}E}{\mathrm{d}c} = \frac{\mathrm{F}nS}{C_{\mathrm{d}}}$$

$\mathrm{d}E/\mathrm{d}c$ in $\mathrm{V\ cm}^3$
D in $\mathrm{s}^{-1}\ \mathrm{cm}^2$

$$D = \frac{1}{C_{\mathrm{d}}R_{\mathrm{d}}}$$

2. ***Finite Length Diffusion for a System with a Reflective Boundary (Reflective Finite Warburg Impedance)***:

In the case of a reaction of a mobile active species distributed in a layer of finite length, terminated by an impermeable boundary, the impedance is analogous to that of an open–circuit-terminated transmission line. For thin homogenous layers of intercalation materials, this type of impedance was observed by Ho et al. (1980).

- Typical shape in complex presentation is shown in Figure 10.
- Impedance function in terms of electric parameters

$$Z(s) = \sqrt{\frac{R_{\mathrm{d}}}{C_{\mathrm{d}}s}}\coth(\sqrt{R_{\mathrm{d}}C_{\mathrm{d}}s}) \qquad (28)$$

- Schematic presentation of the circuit is shown in Figure 11.
- Fit parameters.
  C_{d} in F
  R_{d} in Ω
- Conversion into electrochemical parameters.
  Here S is the geometric electrode area in cm^2, n is the number of electrons participating in the

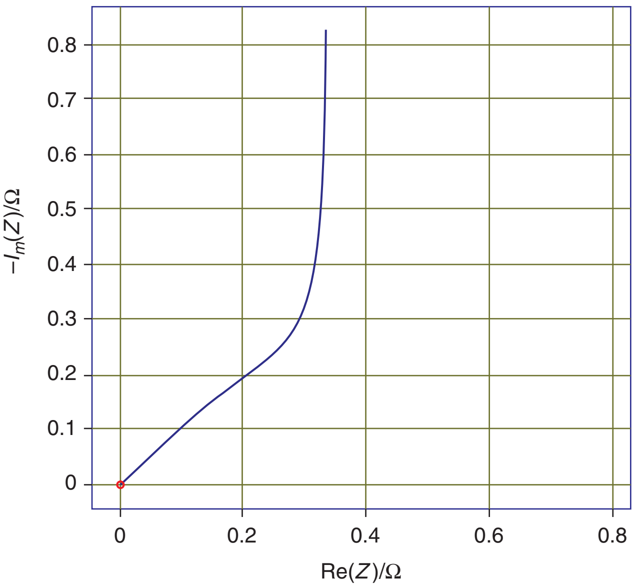

Figure 10. Nyquist plot of an impedance spectrum of open–circuit-terminated transmission line, $R_d = 1\,\Omega$, $C_d = 300$ F, from 10 kHz to 1 mHz.

reaction, and c is the volume concentration in $\mathrm{mol/cm^3}$.

$$\frac{\mathrm{d}E}{\mathrm{d}c} = \frac{\mathrm{F}nS}{C_\mathrm{d}}$$

$\mathrm{d}E/\mathrm{d}c$ in V $\mathrm{cm^3}$
D in $\mathrm{s^{-1}\ cm^2}$

$$D = \frac{1}{C_\mathrm{d}R_\mathrm{d}}$$

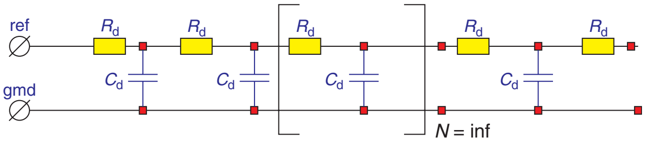

Figure 11. Equivalent circuit of open–circuit-terminated transmission line.

3. ***Finite Length Diffusion with a Conducting Boundary (Transmissive Finite Warburg Impedance)***:
   In the case of a reaction of a mobile active species distributed in a layer with finite length, terminated by a permeable boundary, the impedance is analogous to that of open–circuit-terminated transmission line. This case is realized if the species diffuses through a semipermeable membrane before reaching the electrode interface, or in the case of impedance measurements with a rotating disc electrode, where diffusion length is constant and determined by the rotation speed.

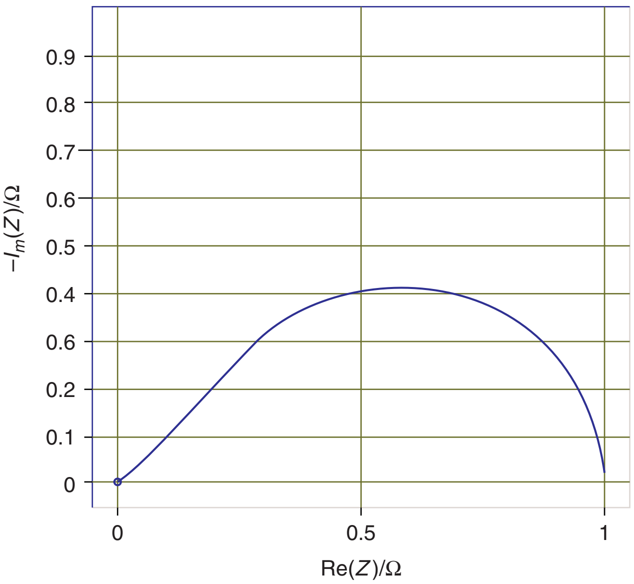

Figure 12. Nyquist plot of an impedance spectrum of finite length diffusion with conductive boundary, $R_d = 1\,\Omega$, $C_d = 10$ F, from 10 kHz to 1 mHz.

- Typical shape in complex presentation is shown in Figure 12.
- Impedance function in terms of electric parameters

$$Z(s) = \sqrt{\frac{R_\mathrm{d}}{C_\mathrm{d}s}}\coth(\sqrt{R_\mathrm{d}C_\mathrm{d}s}) \qquad (29)$$

- Schematic presentation of the circuit is shown in Figure 13.
- Fit parameters.
  C_d in F
  R_d in Ω
- Conversion into electrochemical parameters.
  Here S is the geometric electrode area in $\mathrm{cm^2}$, n is the number of electrons participating in the reaction, and c is the volume concentration in $\mathrm{mol/cm^3}$.

$$\frac{\mathrm{d}E}{\mathrm{d}c} = \frac{\mathrm{F}nS}{C_\mathrm{d}}$$

$\mathrm{d}E/\mathrm{d}c$ in V $\mathrm{cm^3}$
D in $\mathrm{s^{-1}\ cm^2}$

$$D = \frac{1}{C_\mathrm{d}R_\mathrm{d}}$$

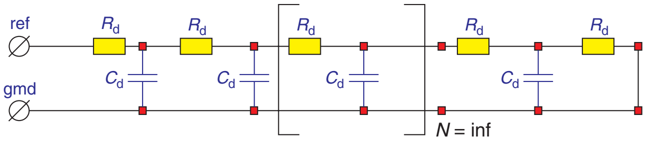

Figure 13. Equivalent circuit of a finite-length transmission line with short-circuit termination.

4. ***CPE***:

Impedance dependence on frequency that is described by the CPE occurs, for example, in many cases of inhomogeneous porous layers and in solid-state conductors. This endemic response function is described below (Macdonald, 1984).

No physical process can result in ideal CPE frequency dependence over the entire range from zero to infinite frequency (except for special values of ϕ such as 0 or 1), although its spectrum is compatible with the Kramer–Kronig transformations (Macdonald and Brachman, 1956). However, in a restricted frequency region, CPE response can be strictly valid. The use of a CPE for analysis is recommended only if there is no way to obtain a more physically relevant model of the process because its ϕ exponent does not usually have a physical meaning. Luckily, however, physically plausible analysis models that include CPE-like behavior over restricted frequency ranges exist and some are discussed in the following section.

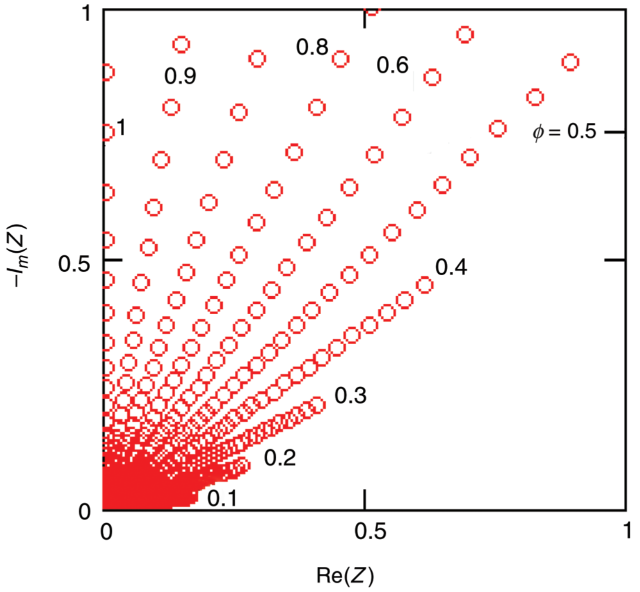

Figure 14. Nyquist plot of a CPE element, $R = 1\,\Omega$, $C = 1$ F, $\phi = 0.4 \ldots 1$.

- Typical shape in complex presentation.
- Impedance function.

$$Z(s) = \frac{1}{Cs^{\phi}} \qquad (30)$$

- Electrochemical parameters conversion.

  No direct conversion is possible. In the case where $\phi > 0.5$, the meaning of C is near to that of a capacitor, while if $\phi < 0.5$, it is nearer to a resistor. For $\phi = -1$, C is an inductance.